CONDENSATION OF GASES ON A COLD SURFACE

by

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ABSTRACT

The purpose of this thesis was to study the rate at which gas molecules will stick on a cryogenically refrigerated surface. The goal was to complete the building of apparatus that could be used to examine this problem, and if possible, to obtain data as to a sticking coefficient for various gases.

The method used was to measure the pressure change in a gas after it was injected into an evacuated chamber which contained a cold surface. The gas that was tested was carbon dioxide.

Due to many problems encountered during this work, it was not possible to obtain the desired data. However, the feasibility of the apparatus is discussed and improvements are suggested.

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INTRODUCTION

The aim of this thesis is to study the condensation of various gases on a cold surface. It is desired to find out if the gas molecules, upon striking such a low temperature surface, will stick to it by condensing.

There are two definite applications for such a study. The first is to help develop high speed gas pumping methods. Cryogenic pumping is being used today to get low pressures, and in order to improve the procedure, it is necessary to know at what rate the remaining gas molecules will stick to the cold surface so that the speed of pumping can be regulated and increased.

The second area of interest is in simulating space conditions (1). For example, the gas molecules of the exhaust of a rocket engine in space will continue to move away from the rocket and will never return. Thus, when testing such an engine here on earth, it is not enough merely to place it in a vacuum, for the exhaust molecules will strike the containing walls of the vacuum system and bounce back to the engine, thereby destroying the space condition, for this could never happen in space. Therefore, some method must be found to prevent these molecules from bouncing back; this can be accomplished by cooling down the bounding surfaces to

low temperatures, so that when the molecules from the exhaust strike them, they will condense. It is desired that the molecules stick to the walls the first time they strike it, and therefore, this thesis will aid in determining whether they will do so.

THEORY

The basic procedure consists of injecting a known number of molecules into a known volume which contains a cold surface, and then seeing how fast the molecules condense; however, other techniques have also been used (2). The number of molecules at any given moment may be determined by measuring the pressure of the gas for, from the perfect gas law, the number of molecules is directly proportional to the pressure.

$$PV = NRT$$

where P = pressure of gas

V = volume of gas

N = number of moles of gas

R = gas constant

T = temperature of gas

Solving for N:

$$N = \frac{V}{RT} P = \text{constant} \times P$$

Finally,

$$\begin{aligned} \text{Number of molecules} &= \text{Avagadro's number} \times N \\ &= \text{Avagadro's number} \times \text{constant} \times P \\ &= \text{constant} \times P \end{aligned}$$

The basic equation which describes the experiment is:

$$\frac{P}{P_i} = e^{-\alpha \frac{A\bar{c}}{4V} t}$$

where P = pressure of gas

P_i = initial pressure of gas

A = area of cold surface

V = volume into which molecules are injected

$\bar{c}$ = mean speed of molecules (at room temperature)

t = time

α = sticking coefficient (probability that a molecule colliding with the area is pumped)

This equation is derived from the following equation for the pumping speed of an orifice or condensing area, which is based on kinetic theory:

$$\frac{dN'}{dt} = -\frac{1}{4} \alpha \frac{N'}{V} \bar{c} A$$

N' = number of molecules

$= LN$

where L is Avagadro's number.

From the perfect gas law,

$$N = \frac{PV}{RT}$$

Therefore

$$N' = \frac{L}{R}\frac{PV}{T}$$

Since $R = kL$, where k = Boltzman's constant,

$$N' = \frac{PV}{kT}$$

and, $\therefore$, $\frac{dN'}{dt} = \frac{V}{kT}\frac{dP}{dt}$ since V and T are constant.

Substituting back into the original equation,

$$\frac{dN'}{dt} = \frac{V}{kT}\frac{dP}{dt} = -\frac{1}{4}\alpha\frac{P}{kT}\bar{c}A$$

or $$\frac{dP}{P} = -\alpha\frac{\bar{c}A}{4V}\,dt$$

Integrating,

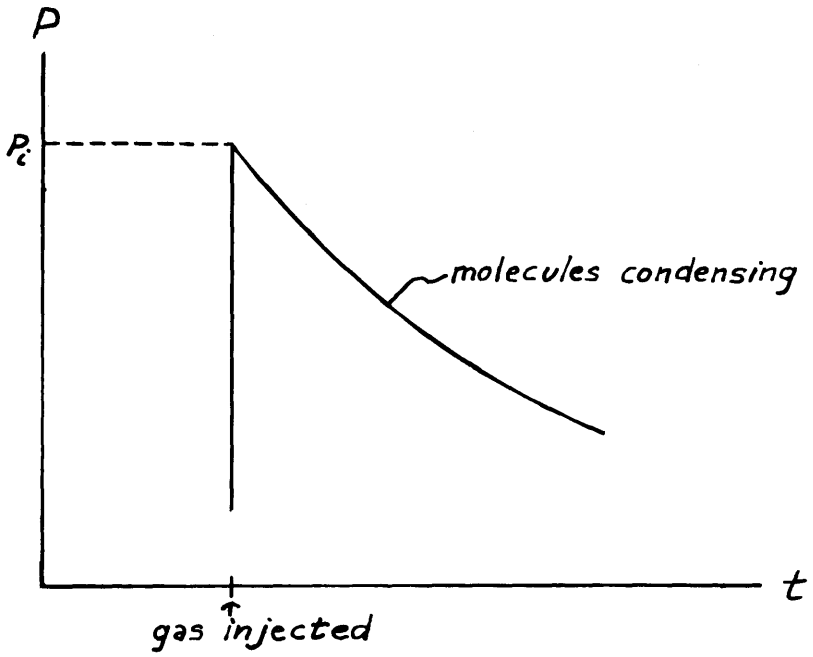
$$\int_{P_i}^{P}\frac{dP}{P} = -\alpha\frac{\bar{c}A}{4V}\int_{o}^{t}dt$$

results in

$$\ln\frac{P}{P_i} = -\alpha\frac{\bar{c}A}{4V}t$$

or $$\frac{P}{P_i} = e^{-\alpha\frac{\bar{c}A}{4V}t}$$

Thus, the purpose of the experiment is to determine this sticking coefficient for different gases. This can be done from a graph of pressure vs. time, since all the other terms are known beforehand. This graph should look something like this:



It is desired that V be much larger than A, for otherwise, the pressure will drop off too fast and it will be difficult to get a meaningful graph. Similarly, P_i should be low enough, for otherwise, the molecules will once again condense at too fast a rate.

APPARATUS

A previous thesis student (3) considered the methods and partially built the apparatus, which I then completed. The entire apparatus is made almost exclusively of glass.

Main system:

The pumping system is made up of a mechanical pump and a diffusion pump (4). As shown in the schematic diagram on page 12, the gas is injected into a cylindrical chamber, and the cold surface is the end of a hollow metal rod which is cooled down by liquid nitrogen. In order to minimize heat conduction to the rod, the metal plate is so constructed that it does not touch the rod. However, because of this, some of the injected gas would be able to escape through the slight opening between the rod and the plate, and therefore, the area above the plate was enclosed so that the amount of escaped gas could be measured. The gas pressures are measured with ion gauges.

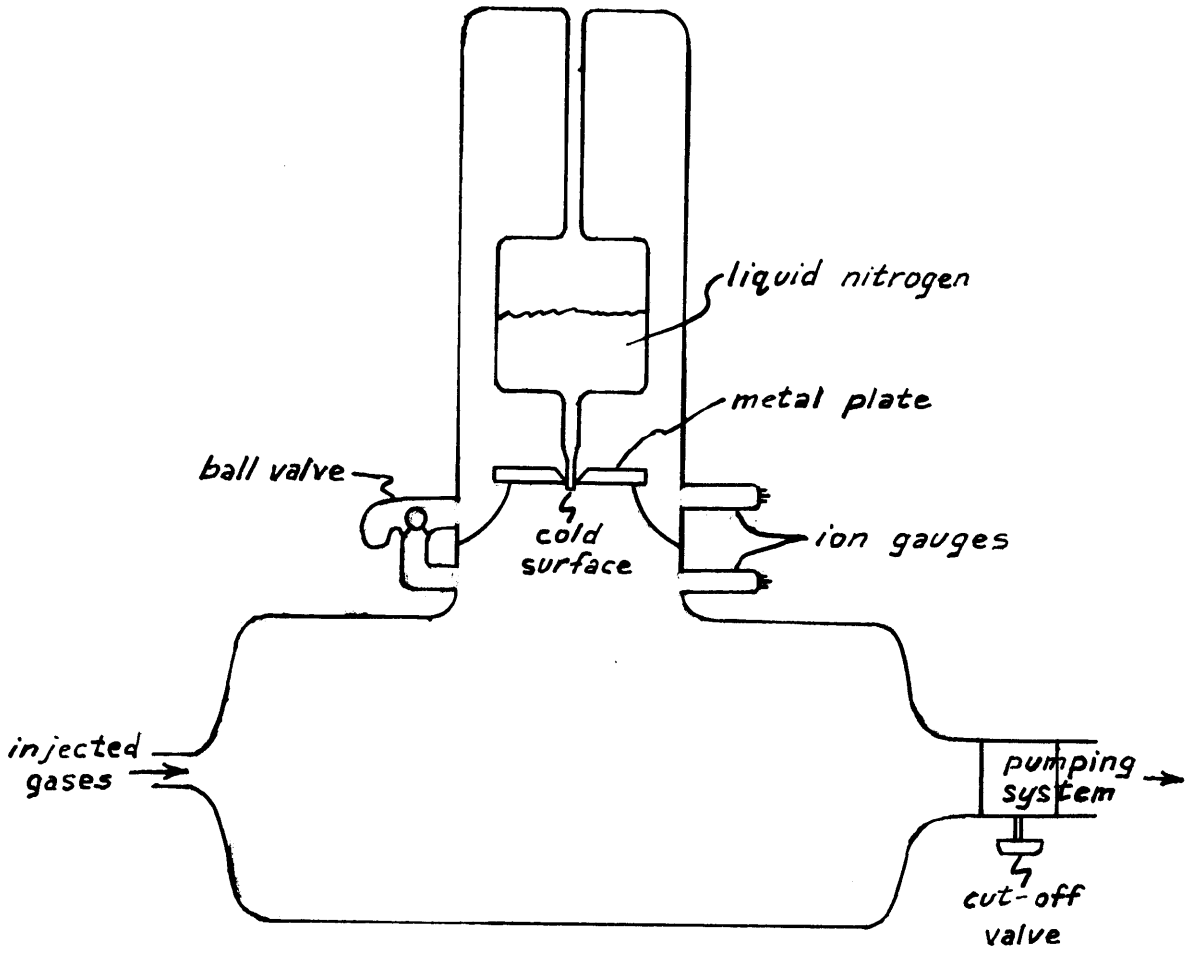
Originally, it was planned to cool the surface with liquid helium, and the apparatus was so constructed. The liquid helium was to be put where the liquid nitrogen is now, and around it was built an insulating pocket which was to be filled with liquid nitrogen. However,

the system as thus constructed did not have sufficient strength to withstand the stresses when it was evacuated. The glass kept on cracking, and therefore, the plan to use liquid helium had to be abandoned; the system was rebuilt to its present state and uses only liquid nitrogen. This severely limits the experiment, for many of the gases which it was originally desired to test will not condense at the temperature of liquid nitrogen (76°K).

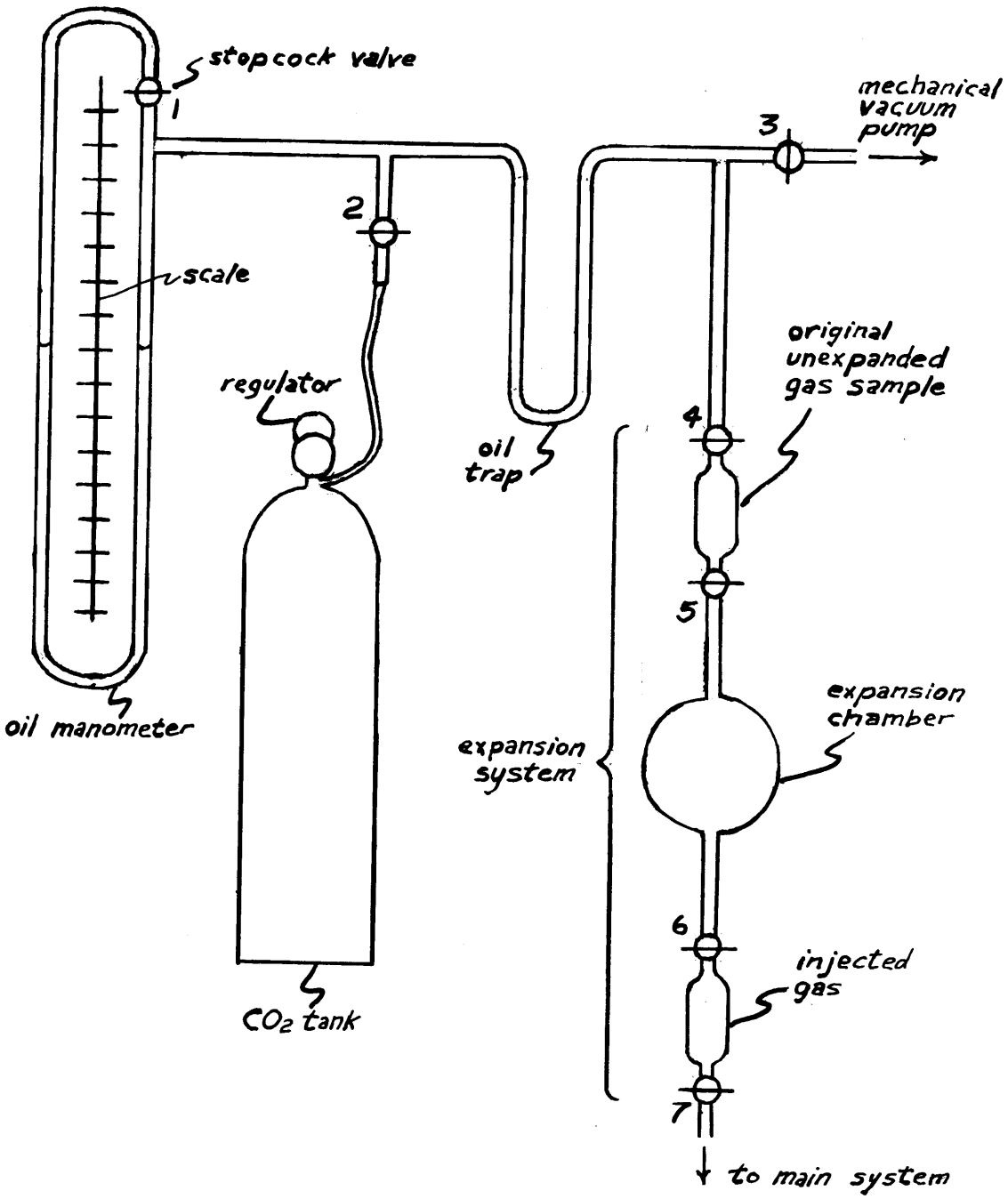
Injection System:

As shown in the schematic diagram on page 13, the pressure of the injected gas is measured by an oil manometer. An expansion chamber was introduced in order that the injected gas would be at a low enough pressure after it expanded again into the main system. A more detailed description follows in the next section.

Main System:


liquid nitrogen
metal plate
ball valve
cold surface
ion gauges
injected gases
pumping system
cut-off valve

Injection System:



PROCEDURE AND DESCRIPTION OF EXPERIMENT

The pressure in the main system and in the expansion system was pumped down to approximately 1×10^{-6} mm Hg. The first gas chosen to be tested was carbon dioxide. As stated before, the choice of gases is limited (5), and furthermore, the vapor pressure of the gas chosen had to be below 1×10^{-6} mm Hg at 76°K (See graph of vapor pressure vs. temperature for some gases on page 16).

The procedure is as follows, with a more detailed one in the appendix: the injection system is evacuated and the desired amount of carbon dioxide is inserted by measuring its pressure with the manometer. A sample of the gas is then taken and expanded in the expansion chamber. A sample of the expanded gas is then taken and injected into the main system. The pressure variation as the gas condenses is measured by the ion gauge and recorded.

Due to the double expansion of the gas, the pressure of the injected gas after it enters the main system, P_i, is 6.5×10^{-6} of its original pre-expanded pressure as measured on the manometer.

The manometer can measure pressures ranging from 1 inch of oil (1.7 mm Hg) to 24 inches of oil, and as a result, P_i can vary from 1.56×10^{-4} mm Hg to 1.11×10^{-5} mm Hg.

Numerous difficulties were encountered during the course of the experiment. Many of them were due to the fact that it was such a large glass system; for example, several leaks developed. The manometer also caused trouble, as the carbon dioxide was apparently diffusing through the oil into the vacuum side of the manometer, and it was difficult to measure the pressure of the carbon dioxide accurately.

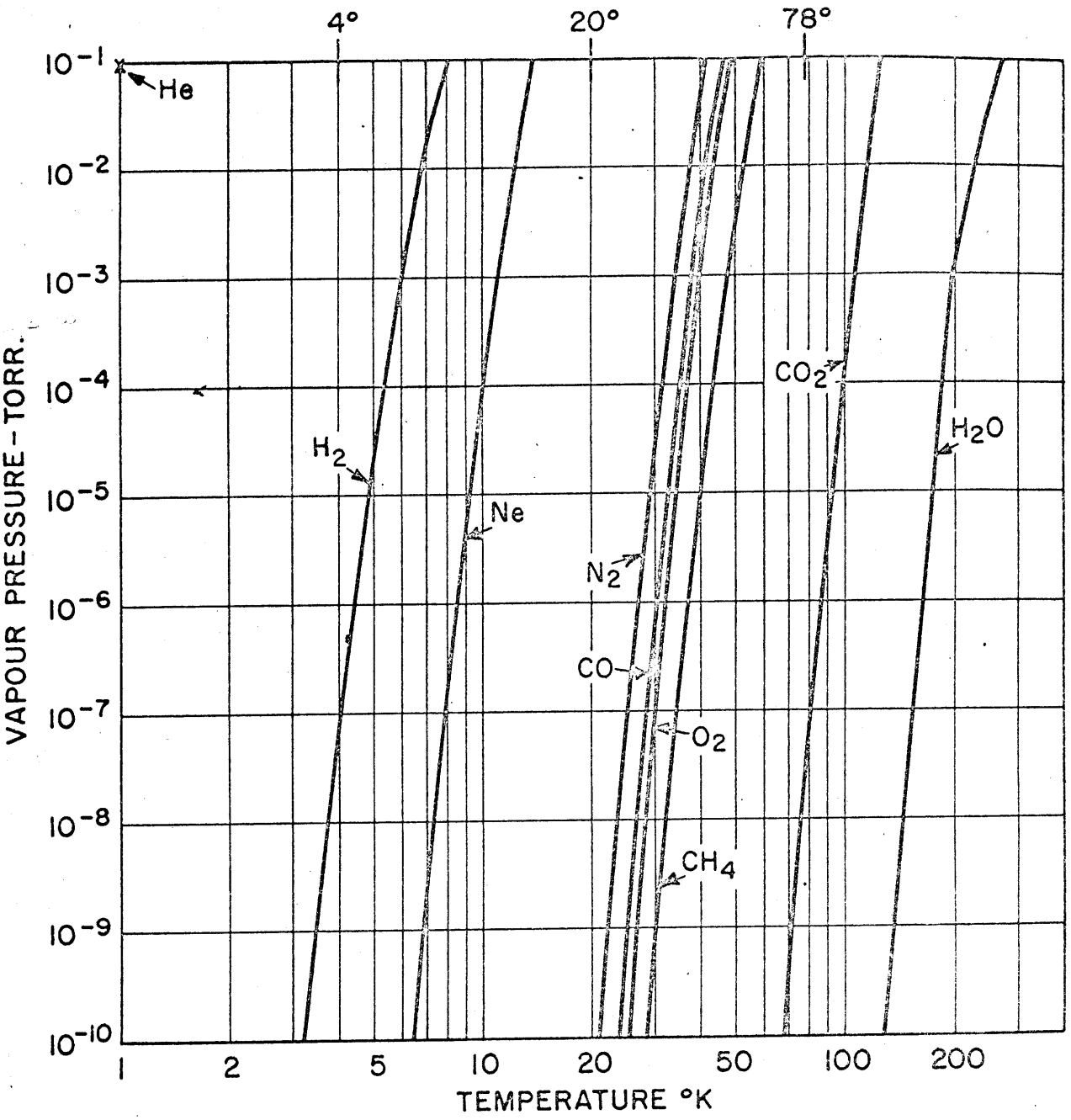


FIG. 1 VAPOUR PRESSURE DATA FOR COMMON GASES

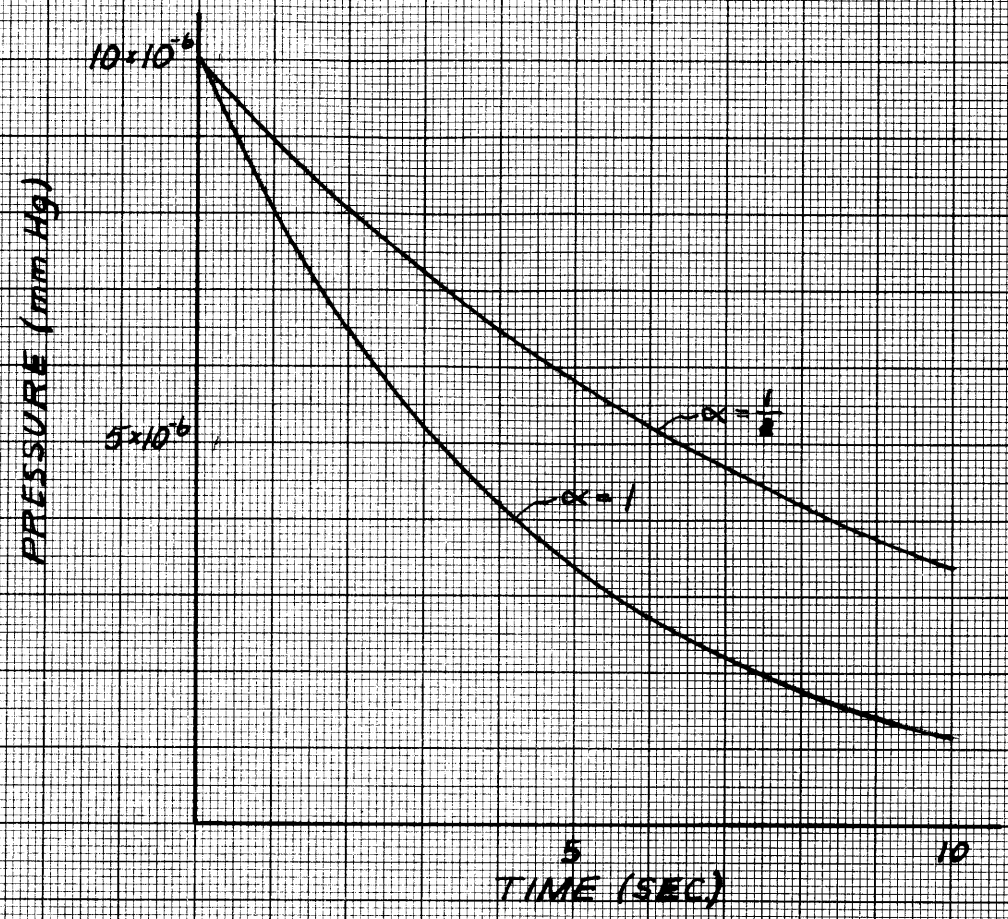
RESULTS

Due to the many problems in building the equipment and running the experiment, there was not enough time to obtain any data.

The only results which were obtained was in testing whether the carbon dioxide would expand as calculated (i.e. without the cold surface in the main system):

Original pressure in main system (when evacuated)	Original pressure of carbon dioxide	Expected P_i	Actual P_i
2×10^{-6} mm Hg	2 cm. oil	1.1×10^{-5} mm Hg	1.2×10^{-5} mm Hg
2×10^{-6} mm Hg	2 cm. oil	1.1×10^{-5} mm Hg	1.0×10^{-5} mm Hg

In order to give some indication of what the results should look like, curves were plotted for the values $\alpha = \frac{1}{2}$ (τ, time constant = 9.23 sec.) and $\alpha = 1$ (τ = 4.62 sec.) on the graph on page 18, with P_i taken to be 10×10^{-6} mm Hg.



PREDICTED CONDENSATION RATES

CONCLUSIONS

One basic problem remains and that is the manometer, as mentioned previously. A solution might be to replace the oil with mercury. To make up for the fact that a mercury manometer could not measure as low pressures as an oil manometer could (the density of mercury is about thirteen times the density of the oil), a second expansion system could be built into the injection system.

Otherwise, it seems feasible that the experiment could be run and the desired data obtained. However, as already indicated, the scope would be very limited due to the fact that liquid helium cannot be used.

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APPENDIX

Manometer Oil:

Octoil-S

specific gravity = 0.9103, 1 inch oil = 1.7 mm Hg

Expansion of Gas:

Volume of unexpanded gas sample = 8.0 cc.

Volume of injected gas sample = 7.6 cc.

Volume of gas after first expansion = 523.8 cc.
(Above two volumes plus volume of expansion chamber)
Volume of main system = 17,300 cc.

The first expansion expands the gas 67.5 times.

The second expansion expands the gas 2,280 times.

The total expansion is therefore 1.536×10^5 times.

Area of Cold Surface:

0.326 $cm.^2$

Planned Detailed Procedure:

Refering to the diagram on page 13,

1) Close valve 4, open valves 5, 6, and 7, and evacuate expansion system through main system. Turn valves 5, 6, and 7 until further turning does not affet the pressure (but leave them open).
2) Open valves 1 and 3, and evacuate rest of injection system with mechanical pump.
3) Close valves 1 and 3.
4) Let in carbon dioxide very slowly by opening valve 2 very slightly. This should force the manometer oil all the way to the top.
5) Open valves 2 and 3, and flood system with carbon dioxide.
6) Close valve 2 and evacuate once again with the mechanical pump.
7) Let in carbon dioxide slowly by carefully opening valve 2 until desired pressure is reached.
8) Take sample of unexpanded gas by closing valve 5 and opening valve 4.
9) Expand gas by closing valves 4 and 7 and opening valve 5.
10) Close cut-off valve on main system (see diagram on page 12).

11) Inject expanded gas into main system by closing valve 6 and opening valve 7; record the pressure variation.